General procedure for the synthesis of compounds 1. To a solution of diphenylvinylphosphane (0.3 g, 1.41 mmol) in Et_2O (10 mL) was added at 0 ºC a solution of the corresponding azide (1.41 mmol) in Et_2O (10 mL). Ten minutes after the end of the addition, the mixture was warmed up to room temperature and stirred for 3 h. In the cases where the appearance of a precipitate is observed, it was filtered and washed with ether (5 mL), whereas in the rest of the cases the solvent was removed under vacuum and the residue was washed with *n*-pentane or *n*-hexane to give **1**.

1a (R^1 = 4-$CH_3C_6H_4$). White solid from *n*-hexane (0.35 g, 79%) that was recrystallized from C_6H_6/*n*-hexane (colorless prisms); mp 112-114 ºC. IR (Nujol) cm^{-1}: 1508, 1322, 1110, 1044, 721, 693. ^1H NMR ($CDCl_3$): δ 2.16 (s, 3H, CH_3), 6.13 (ddd, $^3J_{HaP}$ = 21.8 Hz, $^3J_{HaHc}$ = 18.4 Hz, $^2J_{HaHb}$ = 1.6 Hz, 1H, H_a), 6.22 (ddd, $^3J_{HbP}$ = 36.6 Hz, $^3J_{HbHc}$ = 12.6 Hz, $^2J_{HaHb}$ = 1.6 Hz, 1H, H_b), 6.72 (d, J = 8.0 Hz, 2H, Ar), 6.76 (ddd, $^2J_{HcP}$ = 22.4 Hz, $^3J_{HaHc}$ = 18.4 Hz, $^2J_{HbHc}$ = 12.6 Hz, 1H, H_c), 6.83 (d, J = 8.0 Hz, 2H, Ar), 7.36-7.48 (m, 6H, Ph_2), 7.70-7.78 (m, 4H, Ph_2). ^{13}C {^1H} NMR ($CDCl_3$): δ 20.43 (CH_3), 122.97 (d, $^3J_{CP}$ = 18.1 Hz, C_2), 126.04 (C_4), 128.59 (d, $^3J_{CP}$ = 11.6 Hz, C_m), 129.02 (d, $^1J_{CP}$ = 90.1 Hz, CH), 129.14 (d, $^4J_{CP}$ = 1.5 Hz, C_3), 130.49 (d, $^1J_{CP}$ = 100.7 Hz, C_i), 131.56 (d, $^4J_{CP}$ = 3.0 Hz, C_p), 131.91 (d, $^2J_{CP}$ = 9.6 Hz, C_o), 134.62 (CH_2), 148.27 (d, $^2J_{CP}$ = 3.0 Hz, C_1). ^{31}P {^1H} NMR ($CDCl_3$): δ -0.17. EIMS *m/z* (rel intensity): 318 (M^++1, 22), 317 (M^+, 100), 183 (50). Anal. Calcd for $C_{21}H_{20}NP$: C, 79.48; H, 6.35; N 4.41. Found: C, 79.62; H, 6.47; N 4.25.

1b (R^1 = 4-$CH_3OC_6H_4$). Yellow solid (0.43 g, 92%) that was recrystallized from CH_2Cl_2/Et_2O (yellow prisms); mp 118-120 ºC. IR (Nujol) cm^{-1}: 1508, 1337, 1230, 1118, 1054, 728, 696. ^1H NMR ($CDCl_3$): δ 3.66 (s, 3H, OCH_3), 6.14 (ddd, $^3J_{HaP}$ = 21.8 Hz, $^3J_{HaHc}$ = 18.4 Hz, $^2J_{HaHb}$ = 1.6 Hz, 1H, H_a), 6.24 (ddd, $^3J_{HbP}$ = 41.7 Hz, $^3J_{HbHc}$ = 12.5 Hz, $^2J_{HaHb}$ = 1.6 Hz, 1H, H_b), 6.45 (d, J = 9.0 Hz, 2H, Ar), 6.73 (d, J = 9.0 Hz, 2H, Ar), 6.77 (ddd, $^2J_{HcP}$ = 22.6 Hz, $^3J_{HaHc}$ = 18.4 Hz, $^2J_{HbHc}$ = 12.5 Hz, 1H, H_c), 7.41-7.48 (m, 6H, Ph_2), 7.70-7.78 (m, 4H, Ph_2). ^{13}C {^1H} NMR ($CDCl_3$): δ 55.45 (OCH_3), 114.15 (d, $^4J_{CP}$ = 1.5 Hz, C_3), 123.60 (d, $^3J_{CP}$ = 18.1 Hz, C_2), 128.65 (d, $^3J_{CP}$ = 11.6 Hz, C_m), 129.02 (d, $^1J_{CP}$ = 90.7 Hz, CH), 130.63 (d, $^1J_{CP}$ = 100.7 Hz, C_i), 131.62 (d, $^4J_{CP}$ = 3.0 Hz, C_p), 131.96 (d, $^2J_{CP}$ = 9.6 Hz, C_o), 134.67 (CH_2), 144.37 (d, $^2J_{CP}$ = 3.0 Hz, C_1), 151.78 (C_4). ^{31}P {^1H} NMR ($CDCl_3$): δ -0.77. EIMS *m/z* (rel intensity): 333 (M^+, 70), 318 (100), 183

(23). Anal. Calcd for $C_{21}H_{20}NOP$: C, 75.66; H, 6.05; N 4.20. Found: C, 75.50; H, 6.28; N 4.29.

1c (R^1 = 4-$NO_2C_6H_4$). Yellow solid from *n*-pentane (0.43 g, 88%) that was recrystallized from $CHCl_3$/*n*-pentane (yellow prisms); mp 133-135 ºC. IR (Nujol) cm^{-1}: 1635, 1587, 1446, 1302, 1185, 1114, 843, 754, 634. ^1H NMR ($CDCl_3$): δ 6.20 (ddd, $^3J_{HaP}$ = 22.5 Hz, $^3J_{HaHc}$ = 18.3 Hz, $^2J_{HaHb}$ = 1.3 Hz, 1H, H_a), 6.39 (ddd, $^3J_{HbP}$ = 42.9 Hz, $^3J_{HbHc}$ = 12.4 Hz, $^2J_{HaHb}$ = 1.3 Hz, 1H, H_b), 6.69 (d, J = 9.1 Hz, 2H, Ar), 6.80 (ddd, $^2J_{HcP}$ = 24.0 Hz, $^3J_{HaHc}$ = 18.3 Hz, $^2J_{HbHc}$ = 12.4 Hz, 1H, H_c), 7.46-7.60 (m, 6H, Ph_2), 7.68-7.79 (m, 4H, Ph_2), 7.92 (d, J = 9.1 Hz, Ar). ^{13}C {^1H} NMR ($CDCl_3$): δ 122.29 (d, $^3J_{CP}$ = 20.1 Hz, C_2), 125.53 (d, $^4J_{CP}$ = 2.0 Hz, C_3), 127 (d, $^1J_{CP}$ = 91.5 Hz, CH), 128.27 (d, $^1J_{CP}$ = 101.7 Hz, C_i), 129.20 (d, $^3J_{CP}$ = 12.3 Hz, C_m), 131.94 (d, $^2J_{CP}$ = 9.8 Hz, C_o), 132.62 (d, $^4J_{CP}$ = 2.9 Hz, C_p), 136.44 (CH_2), 138.00 (C_4), 160.06 (d, $^2J_{CP}$ = 3.0 Hz, C_1). ^{31}P {^1H} NMR ($CDCl_3$): δ 6.13. EIMS *m/z* (rel intensity): 348 (M^+, 100), 183 (45). Anal. Calcd for $C_{20}H_{17}N_2O_2P$: C, 68.96; H, 4.92; N 8.04. Found: C, 70.13; H, 4.80; N 8.22.

1d (R^1 = NC-CH_2). Yellow oil (0.37 g, 98%). IR (Film) cm^{-1}: 2239, 1485, 1438, 1396, 1274, 1201, 1119, 727, 699. ^1H NMR ($CDCl_3$): δ 3.96 (d, 2H, $^3J_{HP}$ = 27.6 Hz, CH_2), 6.26 (ddd, $^3J_{HaP}$ = 21.7 Hz, $^3J_{HaHc}$ = 18.4 Hz, $^2J_{HaHb}$ = 1.5 Hz, 1H, H_a), 6.35 (ddd, $^3J_{HbP}$ = 41.5 Hz, $^3J_{HbHc}$ = 12.5 Hz, $^2J_{HaHb}$ = 1.5 Hz, 1H, H_b), 6.69 (ddd, $^2J_{HcP}$ = 23.2 Hz, $^3J_{HaHc}$ = 18.4 Hz, $^2J_{HbHc}$ = 12.5 Hz, 1H, H_c), 7.43-7.58 (m, 6H, Ph_2), 7.63-7.74 (m, 4H, Ph_2). ^{13}C {^1H} NMR ($CDCl_3$): δ 34.03 (d, $^2J_{CP}$ = 5.2 Hz, CH_2), 121.33 (d, $^3J_{CP}$ = 10.1 Hz, CN), 128.81 (d, $^3J_{CP}$ = 11.9 Hz, C_m), 129.03 (d, $^1J_{CP}$ = 91.9 Hz, CH), 129.28 (d, $^1J_{CP}$ = 98.7 Hz, C_i), 131.93 (d, $^2J_{CP}$ = 9.4 Hz, C_o), 132.02 (br s, C_p), 135.37 (CH_2). ^{31}P {^1H} NMR ($CDCl_3$): δ 16.55. EIMS *m/z* (rel intensity): 266 (M^+, 100), 183 (38). Anal. Calcd for $C_{16}H_{15}N_2P$: C, 72.17; H, 5.68; N 10.52. Found: C, 71.99; H, 5.80; N 10.42.

General procedures for the synthesis of compounds 2. **Method A**: A mixture of the corresponding vinyliminophosphorane **1** (0.45 mmol), benzene (15 mL) and the corresponding amine (10 equiv, 4.5 mmol) was stirred for 2-4 h under reflux (N_2) until disappearance of **1** (checked by TLC using silica gel glass plates deactivated with 5% Et_3N in *n*-hexane and AcOEt as eluent). The solvent and the excess of amine was removed in vacuo to give a yellow oily compound. **Method B**: A mixture of **1** (0.45 mmol), benzene (15 mL) and the corresponding amine (1.1 equiv, 0.5 mmol) was stirred for 6 h under reflux (N_2). Then the solvent was evaporated to dryness under reduced

pressure and the residue was washed with *n*-hexane to give a solid or an oil according to the case.

2a (R^1 = 4-$CH_3C_6H_4$, R^2 = R^3 = CH_3). Synthetic method: A. Yellow oil (0.156 g, 96%). IR (Film) cm^{-1}: 1503, 1437, 1326, 1109, 735, 695. ^1H NMR ($CDCl_3$): δ 2.07 [s, 6H, $(CH_3)_2N$], 2.09 (s, 3H, CH_3), 2.45-2.60 (m, 4H, PCH_2CH_2N), 6.56 (d, J = 8.1 Hz, 2H, Ar), 6.74 (d, J = 8.1 Hz, 2H, Ar), 7.32-7.43 (m, 6H, Ph_2), 7.66-7.73 (m, 4H, Ph_2). ^{13}C {^1H} NMR ($CDCl_3$): δ 20.49 (CH_3), 26.79 (d, $^1J_{CP}$ = 70.2 Hz, CH_2P), 44.90 (CH_3N), 52.13 (CH_2N), 122.79 (d, $^3J_{CP}$ = 18.0 Hz, C_2), 126.16 (C_4), 128.76 (d, $^3J_{CP}$ = 11.6 Hz, C_m), 129.31 (C_3), 130.95 (d, $^1J_{CP}$ = 91.7 Hz, C_i), 131.56 (d, $^2J_{CP}$ = 9.3 Hz, C_o), 131.57 (d, $^4J_{CP}$ = 2.1 Hz, C_p), 148.51 (d, $^2J_{CP}$ = 2.8 Hz, C_1). ^{31}P {^1H} NMR ($CDCl_3$): δ 5.77. EIMS *m/z* (rel intensity): 363 (M^++1, 8), 362 (M^+, 30), 302 (30), 291 (100), 183 (50). Anal. Calcd for $C_{23}H_{27}N_2P$: C, 76.22; H, 7.51; N 7.73. Found: C, 76.13; H, 7.65; N 7.82.

2b [R^1 = 4-$CH_3C_6H_4$, R^2 and R^3 = $(CH_2)_4$]. Synthetic method: B. Yellow oil (0.17 g, 97%). IR (Film) cm^{-1}: 1506, 1438, 1326, 1109, 694, 666. ^1H NMR ($CDCl_3$): δ 1.63 (m, 4H, $CH_2CH_2CH_2CH_2$), 2.10 (s, 3H, CH_3), 2.35 (m, 4H, CH_2NCH_2), 2.61-2.67 (m, 4H, PCH_2CH_2N), 6.57 (d, J = 8.0 Hz, 2H, Ar), 6.75 (d, J = 8.0 Hz, 2H, Ar), 7.33-7.45 (m, 6H, Ph_2), 7.67-7.75 (m, 4H, Ph_2). ^{13}C {^1H} NMR ($CDCl_3$): δ 20.53 (CH_3), 23.47 ($CH_2CH_2CH_2CH_2$), 28.27 (d, $^1J_{CP}$ = 69.0 Hz, CH_2P), 48.82 (CH_2N), 53.78 (CH_2NCH_2), 122.84 (d, $^3J_{CP}$ = 18.2 Hz, C_2), 126.15 (C_4), 128.76 (d, $^3J_{CP}$ = 11.4 Hz, C_m), 129.34 (C_3), 131.22 (d, $^1J_{CP}$= 92.5 Hz, C_i), 131.60 (d, $^4J_{CP}$ = 2.9 Hz, C_p), 131.62 (d, $^2J_{CP}$ = 8.8 Hz, C_o), 148.62 (d, $^2J_{CP}$ =2.7 Hz, C_1). ^{31}P {^1H} NMR ($CDCl_3$): δ 5.41. EIMS *m/z* (rel intensity): 388 (M^+, 30), 290 (88), 214 (40), 183 (100). Anal. Calcd for $C_{25}H_{29}N_2P$: C, 77.29; H, 7.52; N 7.21. Found: C, 77.41; H, 7.39; N 7.05.

2c (R^1 = 4-$CH_3OC_6H_4$, R^2 = R^3 = CH_3CH_2). Synthetic method: A. Yellow oil (0.18 g, 98%). IR (Film) cm^{-1}: 1500, 1436, 1329, 1110, 827. ^1H NMR ($CDCl_3$): δ 0.86 (t, J = 7.1 Hz, 6H, CH_3CH_2), 2.42 (q, J = 7.1 Hz, 4H, CH_2CH_3), 2.61 (m, 2H, CH_2), 2.74 (m, 2H, CH_2), 3.67 (s, OCH_3), 6.61 (d, J = 8.7 Hz, 2H, Ar), 6.68 (d, J = 8.7 Hz, 2H, Ar), 7.41-7.50 (m, 6H, Ph_2), 7.75-7.82 (m, 4H, Ph_2). ^{13}C {^1H} NMR ($CDCl_3$): δ 11.79 (CH_2CH_3), 24.94 (d, $^1J_{CP}$ = 66.7 Hz, CH_2P), 44.97 (CH_2N), 46.53 (CH_2CH_3), 55.53 (OCH_3), 114.27 (C_3), 123.40 (d, $^3J_{CP}$ = 17.4 Hz, C_2), 128.68 (d, $^3J_{CP}$ = 11.6 Hz, C_m), 131.44 (d, $^1J_{CP}$ = 93.4 Hz, C_i), 131.47 (d, $^2J_{CP}$ = 9.3 Hz, C_o), 131.49 (d, $^4J_{CP}$ = 2.7 Hz, C_p), 144.77 (d, $^2J_{CP}$ = 2.8 Hz, C_1), 151.79 (C_4). ^{31}P {^1H} NMR ($CDCl_3$): δ 5.56. EIMS *m/z* (rel intensity):

406 (M^+, 49), 306 (98), 230 (60), 183 (100). Anal. Calcd for $C_{25}H_{31}N_2OP$: C, 73.87; H, 7.69; N 6.89. Found: C, 74.02; H, 7.57; N 6.75.

2d [R^1 = 4-$CH_3OC_6H_4$, R^2 and R^3 = $(CH_2)_5$]. Synthetic method: B. Yellow solid from *n*-hexane (0.165 g, 88%). IR (Nujol) cm^{-1}: 1500, 1436, 1335, 1111, 825, 751, 717. ^1H NMR ($CDCl_3$): δ 1.37 [m, 2H, $N(CH_2CH_2)_2CH_2$], 1.50 [m, 4H, $N(CH_2CH_2)_2CH_2$], 2.29 [m, 4H, $N(CH_2CH_2)_2CH_2$], 2.53-2.73 (m, 4H, PCH_2CH_2N), 3.68 (s, 3H, OCH_3), 6.61 (d, J = 9.1 Hz, 2H, Ar), 6.66 (d, J = 9.1 Hz, 2H, Ar), 7.41-7.53 (m, 6H, Ph_2), 7.74-7.80 (m, 4H, Ph_2). ^{13}C $\{^1H\}$ NMR ($CDCl_3$): δ 24.22 [$N(CH_2CH_2)_2CH_2$], 25.85 [$N(CH_2CH_2)_2CH_2$], 25.94 (d, $^1J_{CP}$ = 69.3 Hz, CH_2P), 51.69 (CH_2N), 54.11 [$N(CH_2CH_2)_2CH_2$], 55.57 (OCH_3), 114.30 (C_3), 123.45 (d, $^3J_{CP}$ = 17.4 Hz, C_2), 128.76 (d, $^3J_{CP}$ = 11.4 Hz, C_m), 131.10 (d, $^1J_{CP}$ = 91.8 Hz, C_i), 131.61 (d, $^4J_{CP}$ = 2.6 Hz, C_p), 131.62 (d, $^2J_{CP}$ = 9.1 Hz, C_o), 144.55 (C_1), 151.84 (C_4). ^{31}P $\{^1H\}$ NMR ($CDCl_3$): δ 6.49. EIMS *m/z* (rel intensity): 419 (M^++1, 5), 418 (M^+, 23), 318 (40), 307 (100), 183 (32). Anal. Calcd for $C_{26}H_{31}N_2OP$: C, 74.62; H, 7.47; N 6.69. Found: C, 74.80; H, 7.60; N 6.54.

2e (R^1 = 4-$CH_3OC_6H_4$, R^2 = H, R^3 = $CH_3CH_2CH_2$). Synthetic method: A. Yellow oil (0.17 g, 97%). IR (Film) cm^{-1}: 3278, 1501, 1437, 1331, 1234, 1112, 826, 697. ^1H NMR ($CDCl_3$): δ 0.85 (t, J = 7.3 Hz, 3H, $CH_2CH_2CH_3$), 1.39 (sex, J = 7.3 Hz, 2H, $CH_2CH_2CH_3$), 1.92 (br s, 1H, NH), 2.46 (t, J = 7.3 Hz, 2H, $CH_2CH_2CH_3$), 2.67 (dt, 2H, $^3J_{HH}$ = 7.1 Hz, $^2J_{HP}$ = 11.3 Hz, CH_2P), 2.89 (dt, 2H, $^3J_{HH}$ = 7.1 Hz, $^3J_{HP}$ = 12.3 Hz, CH_2N), 3.68 (s, 3H, OCH_3), 6.63 (d, J = 9.2 Hz, 2H, Ar), 6.68 (d, J = 9.2 Hz, 2H, Ar), 7.42-7.54 (m, 6H, Ph_2), 7.76-7.83 (m, 4H, Ph_2). ^{13}C $\{^1H\}$ NMR ($CDCl_3$): δ 11.70 ($CH_2CH_2CH_3$), 23.06 ($CH_2CH_2CH_3$), 28.64 (d, $^1J_{CP}$ = 72.0 Hz, CH_2P), 43.17 (d, $^2J_{CP}$ = 1.3 Hz, CH_2N), 51.49 ($CH_2CH_2CH_3$), 55.50 (OCH_3), 114.28 (C_3), 123.27 (d, $^3J_{CP}$ = 17.8 Hz, C_2), 128.75 (d, $^3J_{CP}$ = 11.3 Hz, C_m), 131.06 (d, $^1J_{CP}$ = 90.4 Hz, C_i), 131.57 (d, $^2J_{CP}$ = 9.0 Hz, C_o), 131.59 (d, $^4J_{CP}$ = 2.6 Hz, C_p), 144.53 (d, $^2J_{CP}$ = 3.9 Hz, C_1), 151.79 (C_4). ^{31}P $\{^1H\}$ NMR ($CDCl_3$): δ 5.80. EIMS *m/z* (rel intensity): 392 (M^+, 18), 318 (34), 307 (100), 183 (44). Anal. Calcd for $C_{24}H_{29}N_2OP$: C, 73.45; H, 7.45; N 7.14. Found: C, 73.58; H, 7.34; N 7.22.

2f [R^1 = 4-$NO_2C_6H_4$, R^2 and R^3 = $(CH_2)_5$]. Synthetic method: B. Yellow solid from *n*-hexane (0.17 g, 89%). IR (Nujol) cm^{-1}: 1500, 1436, 1335, 1111, 825, 751, 717: ^1H NMR ($CDCl_3$): δ 1.37 [m, 2H, $N(CH_2CH_2)_2CH_2$], 1.47 [m, 4H, $N(CH_2CH_2)_2CH_2$], 2.29 [m, 4H, $N(CH_2CH_2)_2CH_2$], 2.58 (m, 2H, CH_2), 2.72 (m, 2H, CH_2), 6.61 (d, J = 8.9 Hz,

2H, Ar), 7.49-7.59 (m, 6H, Ph_2), 7.73-7.79 (m, 4H, Ph_2) 7.90 (d, J = 8.9 Hz, 2H, Ar),. ^{13}C {^1H} NMR ($CDCl_3$): δ 24.14 [$N(CH_2CH_2)_2CH_2$], 25.80 [$N(CH_2CH_2)_2CH_2$], 26.11 (d, $^1J_{CP}$ = 70.2 Hz, CH_2P), 51.49 (CH_2N), 54.13 [$N(CH_2CH_2)_2CH_2$], 121.95 (d, $^3J_{CP}$ = 19.7 Hz, C_2), 125.55 (C_3), 128.97 (d, $^1J_{CP}$ = 93.4 Hz, C_i), 129.14 (d, $^3J_{CP}$ = 11.6 Hz, C_m), 131.49 (d, $^2J_{CP}$ = 9.9 Hz, C_o), 132.36 (d, $^4J_{CP}$ = 2.3 Hz, C_p), 137.88 (C_4). 160.39 (d, $^2J_{CP}$ = 2.9 Hz, C_1). ^{31}P {^1H} NMR ($CDCl_3$): δ 11.06. EIMS *m/z* (rel intensity): 434 (M^++1, 5), 433 (M^+, 32), 322 (100), 245 (23), 183 (65). Anal. Calcd for $C_{25}H_{28}N_3O_2P$: C, 69.27; H, 6.51; N 9.69. Found: C, 69.40; H, 6.60; N 9.53.

General procedure for the synthesis of compounds 4. A mixture of **1** (0.3 mmol), benzene (15 mL) and **2e** (0.3 mmol) was stirred for 5 days under reflux (N_2) (checked by TLC using silica gel glass plates deactivated with 5% Et_3N in *n*-hexane and AcOEt as eluent). The solvent was evaporated to dryness under reduced pressure, and the crude product was chromatographed on silica gel deactivated with 5% Et_3N in *n*-hexane (elution with AcOEt).

4a (R^1 = 4-$CH_3C_6H_4$, R^2 = 4-$CH_3OC_6H_4$, R^3 = $CH_3CH_2CH_2$). Yellow oil (0.16 g, 77%). IR (Film) cm^{-1}: 1503, 1437, 1327, 1113, 733. ^1H NMR ($CDCl_3$): δ 0.64 (t, J = 7.2 Hz, 3H ,$CH_2CH_2CH_3$), 1.05 (sex, J = 7.2 Hz, 2H, $CH_2CH_2CH_3$), 2.14 (s, 3H, CH_3), 2.15 (m, 2H, $CH_2CH_2CH_3$), 2.44 (m, 4H, CH_2), 2.64 (m, 4H, CH_2), 3.62 (s, 3H, OCH_3), 6.56-6.65 (m, 6H, Ar), 6.79 (d, J = 7.8 Hz, 2H, Ar), 7.38-7.52 (m, 12H, Ph_2), 7.62-7.79 (m, 8H, Ph_2). ^{13}C {^1H} NMR ($CDCl_3$): δ 11.69 ($CH_2CH_2CH_3$), 20.21 ($CH_2CH_2CH_3$), 20.54 (CH_3), 24.82 (d, $^1J_{CP}$ = 65.9 Hz, CH_2P), 24.90 (d, $^1J_{CP}$ = 66.1 Hz, CH_2P), 45.47 (2 CH_2N), 55.57 (OCH_3), 55.61 ($CH_2CH_2CH_3$), 114.38 (C_3), 122.78 (d, $^3J_{CP}$ = 18.0 Hz, $C_{2/2'}$), 123.39 (d, $^3J_{CP}$ = 17.5 Hz, $C_{2/2'}$), 126.11 ($C_{4'}$), 128.73 (d, $^3J_{CP}$ = 11.5 Hz, 2 C_m), 129.37 ($C_{3'}$), 131.45 (d, $^1J_{CP}$ = 93.3 Hz, C_i), 131.53 (d, $^2J_{CP}$ = 9.0 Hz, 2 C_o), 131.54 (m, 2 C_p), 131.60 (d, $^1J_{CP}$ = 93.4 Hz, C_i), 144.87 (br s, C_1), 148.76 (d, $^2J_{CP}$ = 2.6 Hz, $C_{1'}$), 151.86 (C_4). ^{31}P {^1H} NMR ($CDCl_3$): δ 5.16, 5.52. FAB$^+$-MS *m/z* (rel intensity): 710 (M^++1, 16), 709 (M^+, 12), 307 (63), 291 (100), 185 (36), 183 (17). Anal. Calcd for $C_{45}H_{49}N_3OP_2$: C, 76.14; H, 6.96; N 5.92. Found: C, 76.27; H, 7.09; N 5.78.

4b (R^1 = R^2 = 4-$CH_3OC_6H_4$, R^3 = $CH_3CH_2CH_2$). Yellow oil (0.174 g, 80%). IR (Film) cm^{-1}: 1499, 1437, 1330, 1264, 1232, 1112, 912, 827, 697. ^1H NMR ($CDCl_3$): δ 0.64 (t, J = 7.3 Hz, 3H, $CH_2CH_2CH_3$), 1.09 (sex, J = 7.3 Hz, 2H, $CH_2CH_2CH_3$), 2.13 (m, 2H, $CH_2CH_2CH_3$), 2.44 (m, 4H, CH_2), 2.65 (m, 4H, CH_2), 3.64 (s, 6H, OCH_3), 6.57 (d, J =

8.6 Hz, 4H, Ar), 6.62 (d, J = 8.6 Hz, 4H, Ar), 7.37-7.50 (m, 12H, Ph_2), 7.64-7.75 (m, 8H, Ph_2). ^{13}C {^1H} NMR ($CDCl_3$): δ 11.73 ($CH_2CH_2\mathit{C}H_3$), 20.23 ($CH_2\mathit{C}H_2CH_3$), 24.81 (d, $^1J_{CP}$ = 65.7 Hz, CH_2P), 45.50 (CH_2N), 55.59 (OCH_3), 55.61 ($\mathit{C}H_2CH_2CH_3$), 114.41 (C_3), 123.42 (d, $^3J_{CP}$ = 17.4 Hz, C_2), 128.76 (d, $^3J_{CP}$ = 11.5 Hz, C_m), 131.53 (d, $^1J_{CP}$ = 93.4 Hz, C_i), 131.55 (d, $^4J_{CP}$ = 2.9 Hz, C_p), 131.56 (d, $^2J_{CP}$ = 9.0 Hz, C_o), 144.78 (d, $^2J_{CP}$ = 3.3 Hz, C_1), 151.92 (C_4). ^{31}P {^1H} NMR ($CDCl_3$): δ 6.18. FAB$^+$-MS *m/z* (rel intensity): 726 (M^++1, 12), 725 (M^+, 8), 307 (100), 185 (52), 183 (23). Anal. Calcd for $C_{45}H_{49}N_3O_2P_2$: C, 74.46; H, 6.80; N 5.79. Found: C, 74.59; H, 6.67; N 5.90.

4c ($R^1 = R^2$ = 4-$CH_3OC_6H_4$, $R^3 = C_6H_5CH_2$). Yellow oil (0.167 g, 72%). IR (Film) cm^{-1}: 1502, 1438, 1329, 1265, 1231, 1113, 909, 834, 694. ^1H NMR ($CDCl_3$): δ 2.48 (m, 4H, CH_2), 2.70 (m, 4H, CH_2), 3.38 (s, 2H, CH_2Ph), 3.64 (s, 6H, OCH_3), 6.57 (br s, 8H, Ar), 6.90-6.95 (m, 2H, Ph), 7.10-7.14 (m, 3H, Ph), 7.38-7.53 (m, 12H, Ph_2), 7.58-7.69 (m, 8H, Ph_2). ^{13}C {^1H} NMR ($CDCl_3$): δ 25.12 (d, $^1J_{CP}$ = 65.6 Hz, CH_2P), 45.75 (CH_2N), 55.54 (OCH_3), 58.39 (CH_2Ph), 114.37 (C_3), 123.39 (d, $^3J_{CP}$= 17.5 Hz, C_2), 126.91, 128.18, 128.72 (d, $^3J_{CP}$= 11.2 Hz, C_m), 131.46 (d, $^2J_{CP}$= 9.0 Hz, C_o), 131.47 (d, $^4J_{CP}$= 2.9 Hz, C_p), 131.51 (d, $^1J_{CP}$= 93.8 Hz, C_i), 138.37 (q), 144.74 (br s, C_1), 151.85 (C_4), and one not observable CH. ^{31}P {^1H} NMR ($CDCl_3$): δ 5.91. FAB$^+$-MS *m/z* (rel intensity): 774 (M^++1, 15), 773 (M^+, 6), 334 (100), 307 (94), 185 (40), 183 (26). Anal. Calcd for $C_{49}H_{49}N_3O_2P_2$: C, 76.05; H, 6.38; N 5.43. Found: C, 75.91; H, 6.48; N 5.55.

Synthesis of tris(iminophosphorane) 6. To a solution of tris(diphenylphosphinoethyl)amine (0.2 g; 0.31 mmol) in CH_2Cl_2 (15 mL) was added a solution of 4-tolylazide (0.04 g, 0.31 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred for 1.5 h at room temperature (checked by IR until the disappearance of the band of N_3). The solvent was evaporated to dryness under reduced pressure, and the residue was triturated with *n*-hexane. Yellow crystalline **6** was isolated by filtration and dried under vacuum. Yield (0.27 g, 90%); IR (Nujol) cm^{-1}: 1605, 1504, 1439, 1325, 1109. ^1H NMR ($CDCl_3$): δ 2.14 (s, 3H, CH_3), 2.27 (m, 2H, CH_2), 2.46 (m, 2H, CH_2), 6.56 (d, J = 8.0 Hz, 2H, Ar), 6.74 (d, J = 8.0 Hz, 2H, Ar), 7.35-7.49 (m, 6H, Ph_2), 7.58-7.65 (m, 4H, Ph_2). ^{13}C {^1H} NMR ($CDCl_3$): δ 20.58 (CH_3), 25.21 (d, $^1J_{CP}$ = 64.4 Hz, CH_2P), 45.74 (CH_2N), 122.73 (d, $^3J_{CP}$ = 18.0 Hz, C_2), 126.04 (C_4), 128.72 (d, $^3J_{CP}$ = 11.6 Hz, C_m), 129.45 (C_3), 131.49 (d, $^2J_{CP}$ = 8.7 Hz, C_o), 131.49 (C_p), 131.53 (d, $^1J_{CP}$ = 94.5 Hz, C_i), 148.86 (C_1). ^{31}P {^1H} NMR ($CDCl_3$): δ 5.39. EIMS *m/z* (rel intensity): 969 (M^++1, 10),

330 (100), 291 (45), 223 (90), 185 (32), 183 (22). Anal. Calcd for $C_{63}H_{63}N_4P_3$: C, 78.08; H, 6.55; N, 5.78. Found: C, 78.21; H, 6.68; N 5.68.

Synthesis of compound 9b. A mixture of the iminophosphorane **1d** (0.27 g, 1 mmol), diphenylphosphane (0.19 g, 1 mmol) and potassium *tert*-butoxide (0.01 g, 0.1 mmol) in dry THF was stirred at 25 °C for 0.5 h under nitrogen atmosphere. The solvent was removed under vacuum and the residue was chromatographed on silica gel deactivated with 5% Et_3N in *n*-hexane (elution with AcOEt) to give **9b** as a white solid from Et_2O (0.1 g, 47%). IR (Nujol) cm^{-1}: 1436, 1220, 1184, 1164, 1118, 727. ^1H NMR ($CDCl_3$): δ 2.19 (m, 2H, CH_2P), 2.38 (s, 2H, CH_2P), 3.87 (d, $^3J_{HP}$ = 27.3 Hz, 2H, CH_2N), 7.28-7.35 (m, 10H, Ph_2), 7.42-7.59 (m, 10H, Ph_2). ^{13}C {^1H} NMR ($CDCl_3$): δ 19.23 [dd, $^1J_{CP(III)}$ = 15.1 Hz, $^2J_{CP(V)}$ = 4.2 Hz, CH_2P(III)], 25.92 [dd, $^1J_{CP(V)}$ = 69.6 Hz, $^2J_{CP(III)}$ = 16.7 Hz, CH_2P(V)], 33.88 (d, $^2J_{CP(V)}$ = 5.9 Hz, CH_2N), 121.40 (d, $^3J_{CP(V)}$ = 10.2 Hz, CN), 128.60 (d, $^3J_{CP(III)}$ = 6.8 Hz, C_m), 128.71 (d, $^3J_{CP(V)}$ = 11.9 Hz, C_m), 129.07 (C_p), 131.81 (d, $^2J_{CP(V)}$ = 9.3 Hz, C_o), 131.83 (d, $^4J_{CP(V)}$ = 2.8 Hz, C_p), 132.60 (d, $^1J_{CP(V)}$ = 95 Hz, C_i), 132.77 (d, $^2J_{CP(III)}$ = 18.5 Hz, C_o), 137.39 (d, $^1J_{CP(III)}$ = 13.4 Hz, C_i). ^{31}P {^1H} NMR ($CDCl_3$): δ -11.42 [d, $^3J_{PP}$ = 46.3 Hz, P(III)], 24.63 [d, $^3J_{PP}$ = 46.3 Hz, P(V)]. EIMS *m/z* (rel intensity): 452 (M^+, 52), 253 (23), 239 (86), 212 (73), 183 (100). Anal. Calcd for $C_{28}H_{26}N_2P_2$: C, 74.33; H, 5.79; N 6.19. Found: C, 74.18; H, 5.65; N 6.32.

Synthesis of compound 10. To a dry benzene solution (10 mL) of **1b** (0.1 g, 0.3 mmol) was added thiophenol (0.033 g, 0.3 mmol) in dry benzene (5 mL) under nitrogen atmosphere. The solution was stirred at 25 °C for 10 min. The solvent was removed under vacuum and the residue was washed with dry *n*-pentane to give **10** as a colorless oil in quantitative yield. IR (Film) cm^{-1}: 1588, 1505, 1435, 1331, 1114, 830, 736, 698. ^1H NMR ($CDCl_3$): δ 2.72 (m, 2H, CH_2), 3.07 (m, 2H, CH_2), 3.67 (s, 3H, OCH_3), 6.59-6.70 (m, 2H, Ph), 6.65 (d, *J* = 3.6 Hz, 2H, Ar), 7.06-7.16 (m, 3H, Ph), 7.14 (d, *J* = 3.6 Hz, 2H, Ar), 7.32-7.44 (m, 6H, Ph_2), 7.66-7.61 (m, 4H, Ph_2). ^{13}C {^1H} NMR ($CDCl_3$): δ 26.05 (d, $^2J_{CP}$ = 2.1 Hz, CH_2S), 28.58 (d, $^1J_{CP}$ = 63.2 Hz, CH_2P), 55.60 (OCH_3), 114.56 (C_3), 123.58 (d, $^3J_{CP}$ = 17.3 Hz, C_2), 124.19 (C_4'), 128.86 (d, $^3J_{CP}$ = 11.6 Hz, C_m), 129.05 (C_2'/C_3'), 129.14 (C_2'/C_3'), 131.01 (d, $^1J_{CP}$ = 93.0 Hz, C_i), 131.57 (d, $^2J_{CP}$ = 9.1 Hz, C_o), 131.76 (d, $^4J_{CP}$ = 2.8 Hz, C_p), 135.07 (C_1'), 144.46 (d, $^2J_{CP}$ = 2.6 Hz, C_1), 152.20 (C_4). ^{31}P {^1H} NMR ($CDCl_3$): δ 4.97. EIMS *m/z* (rel intensity): 443 (M^+, 25),

333 (63), 318 (72), 307 (100), 183 (51). Anal. Calcd for $C_{27}H_{26}NOPS$: C, 73.11; H, 5.91; N 3.16. Found: C, 73.23; H, 5.80; N 3.80.